

METHOD FOR MANUFACTURING A NANO CARBON MATERIAL AND A WIRING STRUCTURE

FIELD OF THE INVENTION

5 The present invention relates to a method for manufacturing a nano carbon material such as carbon nanotubes and the like and a method for manufacturing a wiring structure using the nano carbon material as wires.

BACKGROUND OF THE INVENTION

10 Nano carbon materials such as carbon nanotubes and the like have recently attracted attention. These nano carbon materials have potential to find applications as electron emission sources of electrodes, conductive films, battery electrodes and the like since they have properties different from those of conventional carbon materials such as graphite and diamond. In addition, nano carbon materials are thought suitable for wiring applications.

15 Vapor phase synthetic and arc discharging methods are known as production (synthetic) methods for nano carbon such as the carbon nanotubes and the like mentioned above.

 Simultaneously, diamond-like-carbon (DLC) and carbon film have been targets of research as novel carbon materials although they are different from the nano carbon materials mentioned above. The DLC and carbon films have previously been produced most

20 commonly by using a vapor deposition method (CVD, PVD), but a method involving electrolytic deposition was recently proposed(Hao Wang and four others, "Deposition of diamond-like carbon films by electrolysis of a methanol solution", US, Applied Physics Letters, August 19, 1996, 69(8), pp. 1074-1076. Yoshikatsu Namba, "Attempts to grow diamond phase carbon films from an organic solution", US, Journal of Vacuum Science Technology,

25 September/October 1992, A10 (5), pp. 3368-3370).

SUMMARY OF THE INVENTION

However, no investigation has been conducted at all to address the technology to manufacture nano carbon materials such as carbon nanotubes and the like using electrochemical means. A vapor phase carbon nanotube synthesis requires a temperature of about 550°C, resulting in enormous production costs and thus limiting the fields of carbon nanotube applications. For example, the vapor phase synthetic method is difficult to apply when trying to form carbon nanotubes directly on a circuit substrate to use them for wiring since allowable temperature limit of the circuit substrate is low.

The present invention was developed to solve the problem described above, and the object of the present invention is to provide a method for manufacturing a nano carbon material and a method for manufacturing a wiring structure, which can be conducted using a simple device and at a low temperature.

The inventors conducted many studies and discovered as a result that a nano carbon material could be manufactured through electrolysis using a simple device and at a lower temperature (for example, ambient temperature) than previously used. That is, to solve the object described above, the present invention is a method for manufacturing a nano carbon material, comprising the step of: forming a nano carbon material on a surface of a metal catalyst by means of electrolysis in an electrolysis solution containing an organic solvent, the semiconductor on which the metal catalyst is unevenly formed being used as a cathode.

In addition, the present invention is a method for manufacturing a nano carbon material, comprising the steps of: forming a metal catalyst unevenly on a surface of a semiconductor by means of electrolysis in an electrolysis solution containing metal catalyst ions, the semiconductor being used as a cathode; and forming a nano carbon material on the surface of said metal catalyst by means electrolysis in an electrolysis solution containing an organic solvent, the semiconductor on which the metal catalyst is unevenly formed being used as a cathode .

Furthermore, the present invention is a method for manufacturing a nano carbon material, comprising the steps of: forming a metal catalyst unevenly on a surface of a semiconductor by etching the metal catalyst on the surface of the semiconductor; and forming a nano carbon material on a surface of the metal catalyst by means of electrolysis in

an electrolysis solution containing an organic solvent, the semiconductor on which the metal catalyst is unevenly formed being used as a cathode.

5 The present invention is a method for manufacturing a wiring structure, comprising the step of: forming a nano carbon material as a wiring between two metal catalysts by means of electrolysis in an electrolysis solution containing an organic solvent, the metal catalysts, which are formed as protrusions on both ends of a wiring forming position, each being used as a cathode and/or an anode.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 shows a pattern diagram of an construction of an electrolysis device preferably used to manufacture the nano carbon material of the present invention.

5 FIG 2 shows a pattern diagram of an embodiment under which a nano carbon material is deposited electrolytically.

FIG 3 shows another pattern diagram of an embodiment under which a nano carbon material is deposited electrolytically.

10 FIG 4(a) is a process diagram showing an embodiment under which a wiring structure of the present invention is manufactured.

FIG 4(b) is a continuation of FIG 4(a).

FIG 5 is another diagram showing an embodiment under which a wiring structure of the present invention is manufactured.

15 FIG 6 is a diagram showing an SEM image of a semiconductor substrate in which Ni is formed unevenly.

FIG 7 is a diagram showing an SEM image of a substrate surface after electrolytic deposition.

FIG 8 is an partially enlarged view of the SEM image of FIG 7.

FIG 9 is an partially enlarged view of the SEM image of FIG 8.

20 FIG 10 is an partially enlarged view of the SEM image of FIG 9.

FIG 11 is a diagram showing an SEM image of another location on the substrate surface after electrolytic deposition.

FIG 12 is an partially enlarged view of the SEM image of FIG 11.

FIG 13 is a diagram showing an TEM image of an electrolytically deposited material.

25 FIG 14 is a diagram showing an TEM image of another measurement region in the electrolytically deposited material.

FIG 15 is an partially enlarged view of the TEM image of FIG 14.

FIG 16 is a diagram showing an SEM image of another substrate surface after electrolytic deposition.

30 FIG 17 is a diagram showing an an SEM image of a substrate surface after electrolytic deposition in a comparative example.

FIG 18 is an partially enlarged view of the SEM image of FIG 17.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The Embodiments of a method of the present invention for manufacturing a nano carbon material is explained below.

5 The method of the present invention for manufacturing a nano carbon material involves the use of a semiconductor on which a metal catalyst is unevenly formed as a cathode and electrolysis conducted in an electrolytic solution containing an organic solvent to form a nano carbon material on the surface of the metal catalyst.

10 The nano carbon material manufactured by the present invention refers to a carbon material comprising a material constructed of pieces from about 0.1 nm to several 100 nm in size. For example, carbon nano-tubes (tubular fibrous materials with a diameter of 0.1 nm to several 10 nm are listed as examples), carbon nano-wires (solid fibrous materials with a diameter of several 100 nm are listed as examples), carbon onions (fine spherical particles with a diameter of several nm to several 100 nm containing several tens to several hundreds
15 of graphite layers arranged in onion-like layers are listed as examples) and carbon nanowire radial aggregates (numerous carbon nanowires are bundled radially and spread like flowers) may be cited. The present invention is particularly suited for manufacturing thin, long fibrous materials such as carbon nanotubes, carbon nanowires and the like.

20 Silicon is readily available and preferred as the semiconductor used in the cathode, but semiconductors such as germanium and the like and high resistance metals may also be used. In addition, when silicon is used, the use of silicon with impurities doped is preferred due to its low electrical resistance.

25 A metal catalyst is formed unevenly on the surface of this semiconductor. Here, the uneven formation refers to the dispersed formation of island shaped and granulated, for example, on the semiconductor surface. The thinking is that the electrically conductive of the formed metal catalyst areas is higher than that of the semiconductor, and the current is concentrated on the areas where the metal catalyst is formed allowing the carbon atoms in the organic solvent present in the electrolytic solution to be deposited electrolytically around the areas where the metal catalyst is formed. Any metal catalyst having electrically
30 conductive may be used. For example, Ni, Co, Fe, Al, Cu and Zn may be listed as examples. Ni, Co and Fe are preferred, and Ni is particularly and most preferred. Co and Fe are preferred next in this order. The formation of a metal catalyst with a thickness of several nm

to several tens of nm, or preferably about 10 nm, on a semiconductor surface is preferred. Now multiple numbers of metal catalysts (for example, Ni and Fe) or alloys thereof may be formed on a semiconductor.

The thinking is that the size of the individual island-like (or granulated) metal catalyst areas formed unevenly on a semiconductor surface determines the type of the nano carbon materials mainly formed on the surface. For example, carbon nanotubes are mainly formed when the size of individual metal catalyst areas (diameter) is 0.1 nm to several 10 nm or preferably 0.1 nm to 10 nm or more preferably from 0.1 nm to 0.5 nm. The thinking is that tubular carbon nanotubes are formed by a so-called edge effect wherein electrolytic current is concentrated on the metal catalyst edge resulting in electrolytic deposition of carbon on said edge while the metal catalyst encounters difficulties undergoing electrolytic deposition in the center. In addition, carbon nanowires are mainly manufactured when the individual metal catalyst areas (diameter) are several 100 nm or preferably from 100 nm to 200 nm. In this situation, the diameter is large enough to allow no edge effect to be manifested, and the electrolytic current flows through the entire metal catalyst surface. Then the carbon is deposited electrolytically on the entire metal catalyst surface resulting in the growth of solid carbon nanowires. In addition when a metal catalyst is present on a semiconductor surface in various sized areas (diameter), various nano carbon materials are formed according to the diameter.

As a method used to form a metal catalyst unevenly on a semiconductor surface, a method wherein an electrolysis is conducted in an electrolytic solution containing metal catalyst ions with a semiconductor used as a cathode, and the metal catalyst is unevenly electrolytically deposited on the semiconductor surface, for example, is available. In this case, the metal catalyst can be formed unevenly by lowering the metal catalyst ion concentration in the electrolysis solution and conducting electrolysis using a low electrical current density. In this case, sufficient metal ions may be dissolved in the electrolysis solution so that the film thickness is about 10 nm when the all of the metal ions dissolved in the solution are accumulated on the substrate surface (on one side). Therefore, the concentration is changed depending on the amount of electrolysis solution and is suitably adjusted along the conditions described above. Solutions obtained by dissolving a nitrate salt of the metal catalysts described above (nickel nitrate, cobalt nitrate, ferrous nitrate and the like) in an alcohol (for example, ethyl alcohol) may be used as the electrolysis solution.

As another method to form a metal catalyst unevenly on a semiconductor surface, a method in which a metal catalyst is formed on a semiconductor surface and this metal catalyst is then etched may be cited. In this case, a metal catalyst such as Ni and the like is formed to a designated thickness by, for example, sputtering on a semiconductor surface, and the surface is subjected to an etching gas (for example, gaseous ammonia) to partially etch and remove Ni.

As a method to control the size (diameter) of the individual metal catalyst areas unevenly formed, the amount of metal ions in an electrolytic solution may be increased to yield large metal catalyst particles in the case of the electrolytic deposition described above. In the case of etching described above, the metal catalyst areas become smaller as the etching temperature rises and the etching time is extended. In either case, the metal catalyst particle size is ordinarily distributed over a relatively broad range, and the particle size of large particles is often several μm while that of small particles is often several nm.

The organic solvent present in an electrolysis solution is not particularly restricted, and alcohols, nitriles, benzenes and xylenes may be listed as examples. Alcohols such as methanol, ethanol and the like and aliphatic nitriles such as methane nitriles, ethane nitriles (acetonitrile) and the like are acceptable. The electrolysis solution may be an organic solvent itself or a mixture of multiple numbers of organic solvents. Furthermore, organic solvents to which water, conductivity aids and the like have been added are also acceptable.

The electrolysis solution described above is electrolyzed in the present invention. The anode is not particularly restricted, and a carbon electrode or a variety of insoluble anodes and the like, for example, may be used. In addition, the electrolysis conditions are not particularly restricted, but a direct current electrolysis using a current density of from 1 mA/cm^2 to several mA/cm^2 or preferably from 2 mA/cm^2 to 6 mA/cm^2 is preferred. The electrolysis voltage (the voltage between the anode and the cathode) changes according to the distance between electrodes and the electrical conductivity of the electrolysis solution, but 0.1 kV to several 10 kV is preferred and 0.1 kV to 5 kV is even more preferred. By raising the electrolysis voltage to this level, the carbon atoms in an organic solvent have the potential to be more readily converted into anions and deposited electrolytically. In addition, an alternating electrolysis is an option, and, in this case, the semiconductor described above may be used in one of the anode and cathode or preferably in both. Now the electrolysis temperature is not particularly restricted, and a temperature at which the electrolysis solution

does not boil, for example, from room temperature to about 50°C may be used. The electrolysis solution may be suitably cooled to remove the heat generated by the electrolysis. The electrolysis time changes according to the electrolysis conditions, but from an hour to about ten hours of electrolysis, for example, is acceptable.

5 The electrolysis device shown in Figure 1, for example, may be used to conduct the electrolysis. In this figure, the electrolysis device (10) is equipped with an electrolysis cell (2), a magnetic stirrer (3), an cathode (4) comprising a semiconductor substrate, a anode (6), a thermometer (7) and a DC power source (8). An electrolysis solution containing an organic solvent is present inside the electrolysis cell (2). A metal catalyst (4a) is unevenly formed on
10 the surface of the cathode (4) facing the anode (6). The electrolysis results in electrolytic deposition of carbon atoms from the organic solvent on the metal catalyst (4a) and growth toward the anode (6).

 The nano carbon material electrolytically deposited may be mechanically peeled from the metal catalyst, for example, and recovered. In addition, nano carbon materials
15 encapsulating the metal catalyst or nano carbon materials formed with the metal catalyst on the bottom may be obtained. Also, the nano carbon material may be used as it is electrolytically deposited on the semiconductor.

 The conditions under which a nano carbon material is electrolytically deposited are shown schematically in Figures 2 and 3. In Figure 2, a metal catalyst (40a) is formed in the
20 shape of islands on the surface of a semiconductor substrate (40), a nano carbon material extends toward the cathode (upward in the figure) from the edge of the metal catalyst (40a) by the edge effect described above and forms tubular carbon nanotubes. In addition, in Figure 3, an island-shaped metal catalyst (41a) is formed on the surface of a semiconductor substrate (41), and a nano carbon material is electrolytically deposited on the entire surface
25 (including the side surface) of a metal catalyst (40a) forming a carbon onion encapsulating the metal catalyst.

 Next, one embodiment of method for manufacturing a wiring structure of the present invention is explained. The method for manufacturing a wiring structure of the present invention is conducted using the same procedures used to manufacture the nano carbon
30 materials described above, but the difference from the method described above is the use of a metal catalyst formed as protrusions from both ends of a wiring formation location as the anode and the cathode. In the method for manufacturing a wiring structure of the present

invention, a nano carbon material is formed as wiring on the metal catalyst between the areas acting as the anode and the cathode. This point will be explained with reference to Figure 4.

In Figure 4, wiring patterns 200 and 201 [Figure 4(a)] are individually formed on the surfaces of two circuit substrates 100 and 101. Let us assume that the end (right end) of the wiring pattern 200 needs to be connected to the end (left end) of the wiring pattern 201. In this case, protrusions 200a and 201a each comprising a metal catalyst are already formed along with the end of the wiring pattern 200 (right end) and the end of the wiring pattern 201 (left end) forming both ends of the wiring formation location. Next, the wiring formation location described above containing at least the protrusions 200a and 201a is immersed (or brought in contact) in an electrolysis solution containing an organic solvent. In this case, the entire individual circuit substrates 100 and 101 may be immersed, or an electrolysis cell that immerses only the wiring formation locations described above in the electrolysis solution may be used.

When an electrolysis is conducted using protrusions 200a and 201a as the cathode and anode, respectively (either may be the cathode but the protrusion 200a is arbitrarily designated as the cathode in this embodiment), under this condition, the nano carbon material electrolytically deposited on the protrusion 200a grows toward the protrusion 201a and the nano carbon material connects to the protrusion 201a in due course. The nano carbon material forms a wiring 300 between protrusions 200a and 201a in the manner described. [Figure 4(b)] Now the electrolysis may be conducted using direct current or an alternating current electrolysis may be conducted. Actually, the protrusion 200a is electrically conducted to the wiring pattern 200 and the protrusion 201a is conducted to the wiring pattern 201, the power source may be connected to the individual wiring patterns 200 and 201 for the electrolysis. When a direct current electrolysis is conducted, an insoluble metal or a carbon material is preferably formed as an electrode on the protrusion on the anode side.

The size (diameter) of protrusions 200a and 201a may be comparable to the size (diameter) of the metal catalyst in the nano carbon material production method described above. By controlling the diameter, the same point at which the type of nano carbon material is changed in the nano carbon material production method described above is observed. The height of protrusions 200a and 201a may be, for example, several nm to several 10 nm. Essentially, the current should be concentrated on protrusions 200a and 201a.

Next, another embodiment of the wiring structure production method is explained with reference to Figure 5. In Figure 5, a protrusion 210a is formed on a wiring pattern 210, and a protrusion 211a is formed on a wiring pattern 211. Now the wiring patterns 210 and 211 are positioned facing each other, and a wiring structure needs to be formed between protrusions 210a and 211a. Now in this figure, the wiring pattern 210 is positioned on top of the wiring pattern 211, and the protrusion 210a is located on the extension of the protrusion 211a.

When a power source is connected to individual wiring patterns 210 and 211 and an electrolysis is conducted while at least the space between the protrusions 210a and 211a is filled with the electrolysis solution described above, a nano carbon material is formed in the form of a wiring 301 between the protrusions 210a and 211a in the same manner observed in the Figure 4 described above. Now a nano carbon material forms a wiring structure even when it is slightly off from the extensions from the protrusions 210a and 211a.

As described above, a wiring structure can be formed at a low temperature such as ambient temperature and the like using a nano carbon material when a method for manufacturing a wiring structure of the present invention is used. In addition, fine wiring formation that was extremely difficult to obtain previously can be easily conducted. That is, a current concentrates on a protrusion in a wiring formation location, and a nano carbon material can be selectively electrolytically deposited on the areas where wiring is desired.

(Examples)

Next, the present invention is explained in further detail by presenting specific examples below, but the present invention is not limited to these examples.

<Example 1>

1. Metal Catalyst Formation on Semiconductor Surface.

Ni was sputtered to a thickness of 30 nm on the surface of a semiconductor substrate (resistance ratio: 0.5 Ωcm , electrode area 50 mm^2) consists of p type crystalline silicon and was left standing for ten minutes in a gaseous ammonia atmosphere. This treatment yielded a semiconductor substrate from which a portion of the Ni was etched and removed, leaving granular Ni. The SEM (scanning electron microscope) image of the semiconductor substrate on which Ni was unevenly formed is shown in Figure 6. The white area in the figure shows granular Ni. The majority of the granular Ni was about 0.1 μm to 0.5 μm in size (diameter),

but the presence of granular Ni areas several 10 nm in diameter was also confirmed when the magnification of the SEM image was increased (not shown in the figures). The semiconductor substrate prepared using this etching method was labeled substrate (1).

2. Electrolytic Deposition on cathode Using Electrolysis.

5 The electrolysis device shown in the aforementioned Figure 1 was prepared. The substrate (1) described above was used as the cathode. A carbon rod with an external diameter of 5 mm was used as the anode. Fifty milliliters of methane nitrile (purity 99.5% by volume, reagent special grade) was used as the electrolysis solution, and an electrolysis was conducted using a current density of 4 mA/cm², a distance between electrodes of 5 mm, an
10 electrolysis voltage of 1 kV and an electrolysis solution volume of 50 ml to obtain an electrolytically deposited material on the cathode surface. The electrolysis was conducted at room temperature, and the solution temperature rose only 2°C to 3°C after the electrolysis.

<Example 2>

15 In this example, the uneven deposition of Ni on the semiconductor substrate described above and a nano carbon material electrolytic deposition were conducted simultaneously in the electrolysis solution described below.

 First, 4.4×10^{-2} mg of Ni nitrate was dissolved in 2.5 ml of ethanol (purity 99.5% by volume, reagent special grade), and the solution was dissolved in 50 ml of ethanol to prepare
20 an electrolysis solution. An electrolysis was conducted using electrolysis conditions identical to those described in Example 1 and an electrolytically deposited material was obtained on the cathode surface using the electrolysis solution and the electrolysis device described above, using the semiconductor substrate described above as the cathode and the carbon rod described above as the anode. The electrolysis time was eight hours. The thinking is
25 that granular Ni was deposited on the semiconductor substrate in the initial stage and a nano carbon material was electrolytically deposited next on the Ni granules in this electrolysis.

<Comparative Example>

 An electrolysis was conducted and an electrolytically deposited material was obtained
30 using the same procedure described in Example 1 above with the exception that Ni was not formed on the semiconductor substrate described above and ethanol was used as the electrolysis solution.

The electrolytically deposited materials obtained in the individual examples and the comparative example were identified according to the following method. First the SEM (scanning electron microscope: manufactured by Nippon Denshi JSM-5600, electron beam 15 kV) images of the cathode containing the electrolytically deposited material obtained was examined, and, in addition, TEM (transmittance type electron microscope: manufactured by Nippon Denshi, JEM-2010F, electron beam 200 kV) images of the electrolytically deposited material were examined. In addition, EDS (energy dispersive spectroscopy: an energy dispersing type X ray diffraction device, manufactured by Oxford, Link ISIS, electron beam 15 kV) measurements were taken in the same measurement zone as the SEM measurements described above. The results are shown in Figures 7-18 and summarized in Table 1.

First, Figure 7 is an SEM image of the substrate surface obtained in Example 2 after electrolytic deposition, Figure 8 is a partially enlarged view of the SEM image of Figure 7, Figure 9 is a partially enlarged view of the SEM image of Figure 8, Figure 10 is a partially enlarged view of the SEM image of Figure 9. In each figure, white areas represent deposited materials and black areas represent accumulations of amorphous carbon films. These deposited materials showed spike-like (needle-like) growths using designated sections of the semiconductor substrate as the nucleus.

Figure 11 is an SEM image of another location on the substrate surface obtained in Example 2 after electrolytic deposition, and Figure 12 is a partially enlarged view of the SEM image of Figure 11. In each figure, white sections represent deposited materials, and the deposited materials show fibrous growths. Furthermore, an elemental analysis was conducted using EDX on the same measurement zones for the measurements shown in Figures 7 and 11 described above, and the white areas in individual figures were found to be carbon. The Figures 7 through 12 above indicate that fibrous carbon type materials with a diameter of about 100 nm are formed in Example 2, and they can be referred to as carbon nanowires.

Figure 13 is a TEM image of the electrolytically deposited material of Example 2. This figure showed that an onion-shaped carbon material constructed from multiple laminated graphite layers was formed. In addition, the results of the EDX analysis described above indicated that the material was composed of carbon, and the conclusion was that this deposited material was a carbon onion.

Figure 14 is a TEM image of the electrolytically deposited material of Example 2 in the measurement zone different from that shown in Figure 13, and Figure 15 is an partially enlarged view of the TEM image of Figure 14. According to Figure 15, this fibrous deposited material contained multiple laminated layers of graphite with a hollow core. According to Figure 15, the distance between individual graphite layers was about 0.33 nm to 0.36 nm, the external diameter was about 30 nm and the internal diameter was about 2 nm. The distance between layers in carbon nanotubes is ordinarily 0.34 nm, and this deposited material can be identified as carbon nanotubes based on the data.

Figure 16 is an SEM image of the substrate surface from Example 1 after electrolytic deposition, and spikes of electrolytically deposited material using Ni as the nucleus were observed in the area slightly to the right of center of the figures. This electrolytically deposited material was also identified as carbon using EDX and was thought to be carbon nanowire.

Figure 17 is an SEM image of the substrate surface from the Comparative Example after electrolytic deposition, and the white and black areas in the figure both represent amorphous carbon film. The thinking is that the difference in the film thickness (irregularity of film surface) projects white and black areas. In addition, Figure 18 is an partially enlarged view of the SEM image of Figure 17. A film-like material was deposited over almost the entire substrate surface, but fibrous carbon materials such as carbon nanotubes, carbon nanowires and the like were not observed. Now this film-like material was examined using Raman spectroscopy, and no sharp signals associated with diamond-like carbon were observed. The thinking was that the film was composed of amorphous carbon.

The results mentioned above are summarized in Table 1.

Table 1

	State of metal catalyst	Electrolysis solution	Electrolytically deposited material		
			Carbon nanotube	Carbon nanowire	Carbon onion
Example 1	Uneven (etching method)	Methane nitrile	Unconfirmed	Present	Unconfirmed
Example 2	Uneven (electrolytic method)	Ethanol	Present	Present	Present
Comp. Ex.	None	Methane nitrile	Absent	Absent	Absent

As clearly indicated by the data presented in Table 1, carbon nanotubes, carbon nanowires and carbon onions were obtained in Examples 1 and 2. In the case of the comparative example, amorphous carbon film layers were obtained, but no carbon nanotubes or carbon nanowires were obtained.

- 5 According to the method for manufacturing a nano carbon material of the present invention , a nano carbon material can be manufactured using a simple electrolytic method using a simple device and at a lower temperature (for example, ambient temperature) than previously used, and the method is particularly suited for manufacturing fibrous nano carbon materials such as carbon nanotubes, carbon nanowires and the like.